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## RECENT METHODS IN ELEMENTARY ORGANIC ANALYSIS.

(ABSTRACT.)

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IN THE paper a careful study was made of the Dennstedt, Morse and Walker methods of determining carbon, hydrogen and nitrogen in organic compounds. In the Dennstedt method (compare *Ber. d. Deut. Chem. Ges.*, vol. 30, p. 1590; vol. 38, p. 3729; vol. 39, p. 1623; Dennstedt's *Anleitung zur Vereinfachten Elementaranalyse*) three applications of chlorplatinic acid were found necessary in order to prepare the quartz properly for the combustions. The results on nitrogen, which is determined simultaneously with the carbon and hydrogen by absorbing the nitrogen tetroxide with lead dioxide and weighing as lead nitrate, were low, and there is evidently greater difficulty in obtaining concordant results than by the other two methods.

The Morse method was carried out as described by the author (*Am. Chem. J.*, vol. 33, p. 457; *Exercises in Quan. Chemistry*, p. 457, H. N. Morse). The objectionable feature is that it does not permit of the determination of nitrogen.

In the history of chemical science no portion is of greater interest than the one which concerns itself with the development of our present system of elementary organic analysis.

Lavoisier was the first chemist to reduce the subject to a quantitative basis. By his experiments he established the true principles of combustion, which furnished a basis for the determination of the composition of organic compounds. Working on the principle that oxygen united with carbon and hydrogen to form permanent compounds, Lavoisier succeeded in determining the quantitative composition of some organic compounds. His first work was done with crude apparatus, but his results were quite accurate, when the process which he employed is taken into consideration. Lavoisier improved his methods very rapidly and devised methods which are very similar to those in use at the present time. He succeeded in analyzing substances which were difficult to burn, and obtained good results.

It would be difficult to estimate too highly the significance of his work. He established the fundamental principles of elementary

organic analysis and devised methods by which these principles could be used in quantitative determinations.

But little was done after the death of Lavoisier until 1806, when Saussure, Thénard and Berthollet made an attempt at organic analysis. Their method was essentially one of mixing the substances to be analyzed, in the form of a vapor, with oxygen and exploding the mixture or decomposing the substance at a high temperature. By this means they succeeded in converting the carbon and hydrogen into permanent gaseous compounds. With many substances they obtained good results.

The next modification of the process was made by Gay-Lussac and Thénard. They continued the process of Lavoisier, but used potassium chlorate as an oxidizing agent. A definite quantity of the substance to be analyzed was mixed with potassium chlorate, and the mixture heated. They obtained some good results for carbon and hydrogen. In the nitrogen determination they used copper oxide. The results obtained were good with a small number of substances.

Berzelius continued the work, using Lavoisier's plan. He used potassium chlorate as an oxidizing agent. The activity of the action was modified by the addition of sodium chloride.

The work of Liebig (1823-1830) is considered to be the most important contribution from the time of Lavoisier to the present. Liebig succeeded in perfecting the first process that would produce satisfactory results. Liebig used a hard glass tube about 18 inches long and 0.5 inch in diameter. The tube was closed at one end, the closed end being drawn out to a sharp tip. The tube was charged for a few inches with granular copper oxide. The weighed substance was added, mixed with fine copper oxide. The tube was then filled with copper oxide. Calcium chloride was used to absorb the water, and potassium hydroxide to absorb the carbon dioxide. The tube was heated in a charcoal furnace. To remove all the gas from the tube an aspirator was attached to the potassium hydroxide bulbs, the tip of the closed end of the combustion tube was broken off and dry air allowed to enter. Liebig succeeded in making satisfactory nitrogen determinations.

Liebig's process, with a few modifications, is the one in general use at the present time. The substance can be completely burned, and if sufficient care is exercised satisfactory results are obtained.

The furnace used at present is provided with a tube open at both ends. Through the rear end dry oxygen is admitted. At the opposite end the absorption apparatus is attached. A tile furnace is used, and heat is supplied by means of gas burners.

The following references were used in this historical sketch: Quantitative Chemical Analysis, Julian, p. 295; Organischen Chemie, Meyer and Jacobson, p. 19; Treatise on Chemistry, Roscoe and Schorlemmer, vol. 3, p. 40.

For a long time there have been objections to the old form of combustion furnace which is used in elementary organic analysis. The furnace is expensive, it is heavy and requires a large amount of table space. Much time is required in heating and cooling it. If a small room is used the temperature soon becomes too high for comfort. The quantity of gas used in heating the furnace and the amount of oxygen consumed are both so large that methods which will be less expensive than this one are very desirable. The old form of furnace does not allow the flame to come near the tube. The more recent methods aim to secure as near as possible direct effects of the heat. Because of these facts simple and less expensive apparatus have been designed.

Three of the more recent and most inviting methods proposed were tested by the writer and the results were compared with those obtained by the older method.

#### I. DENNSTEDT'S METHOD.

The first of the new methods employed was the one generally known as Dennstedt's method, the apparatus having been designed and carefully tested by Prof. Max Dennstedt, of Hamburg. Professor Dennstedt's papers on the subject are to be found in *Berichte der deutschen Chemischen Gesellschaft*, as follows: Vol. 30, page 1590; vol. 38, page 3729; vol. 39, page 1623.

A very carefully prepared paper has been published by Professor Dennstedt under the title of "*Anleitung zur Verinfachten Elementaranalyse*."

The characteristic features of this method are that platinized quartz is used in the combustion tube without copper oxide, and that the nitrogen is determined by means of lead peroxide at the same time that carbon and hydrogen are determined.

This furnace has many desirable features. It costs but little, it is easy to handle, is easily heated and cooled, and requires less gas than the old form. Good results are said by some to be obtained by experienced operators; by others the method is considered unsatisfactory. I succeeded in getting a few good results for carbon and hydrogen, but in spite of prolonged attempts and variation of methods I did not succeed in getting a satisfactory result for nitrogen, as will be seen in examining the table.

References on the above method are as follows: *Anleitung zur*

Vereinfachten Elementare Analyse, by Max Dennstedt. *Der deutschen Chemischen Gesellschaft, Berichte*, vol. 30, page 1590; vol. 38, page 3729; vol. 39, page 1623. *Organische Verbindungen*, by Carl Meyer, page 117.

## II. MORSE'S METHOD.

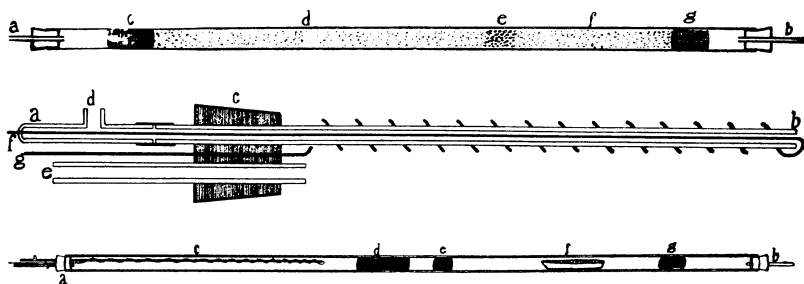
The second method used in the test was what is known as Morse's method. This method was first used by Prof. H. N. Morse of Johns Hopkins University. The original paper on the subject is to be found in the *American Chemical Journal*, vol. 33, page 457. The principal feature of the method is that the forward part of the tube is heated entirely by means of a hot platinum wire spiral on the inside of the tube.

A tube of hard glass 15 mm. in diameter and 70 cm. long is used. Into one end of the tube is fitted a two-hole rubber stopper. Through one hole in the stopper is put a porcelain or quartz tube 250 mm. long and 6 mm. in diameter. The bore of the tube should be just large enough to admit a No. 14 wire loosely. The other hole of the rubber stopper is used for the calcium chloride tube of the absorption apparatus. The quartz tube is allowed to project about 25 mm. outside of the rubber stopper. A piece of No. 14 platinum wire about 10-12 cm. long is united to a piece of No. 28 or 29 platinum wire about 175 cm. long. The piece of coarse wire is placed inside the tube so that the union of the two wires is 3-4 cm. on the inside. Removed from the rubber stopper the fine wire extends through the tube to the inner end, and is then wrapped about the quartz tube in small even-loops back to within 3-4 cm. of the rubber stopper. Here union is made with another piece of No. 14 platinum wire which leads through the stopper. A small glass T tube 6 mm. in diameter is joined to the quartz tube by means of a piece of rubber tubing. Through one opening the platinum wire leads, and through the other the stream of oxygen enters. The opening through which the platinum wire leads must be sealed. It is very necessary that the platinum wire does not come into contact with the walls of the combustion tube. In case it does make direct contact it will adhere to the sides of the tube as soon as it is heated.

Just behind the quartz tube and platinum spiral there is placed a 10-cm. spiral of reduced copper-wire gauze. Back of this reduced copper-wire gauze is a 7-cm. spiral of well oxidized copper-wire gauze, and behind this spiral of oxidized copper is the porcelain boat containing the substance to be analyzed. Behind the boat is a small spiral of copper-oxide gauze. The distance between the

boat and the spirals of oxidized copper is determined by the nature of the substance in the boat.

The tube can be supported by clamps, or, what is still better, a sheet-iron trough lined with asbestos paper, as described in part I of this paper. The whole apparatus can be mounted on sheet-iron supports. The following diagrams represent the relationship of the parts:



### III. WALKER'S METHOD.

The third method employed in conducting this comparative test was what is known as Walker's method, the apparatus having been designed and used under the directions of Prof. James Walker, of the University College of Dundee.<sup>1</sup>

The most significant feature of this method is that the size of the furnace is greatly reduced and simplified. The apparatus is a modification of the apparatus used in the Dennstedt process, the only essential difference being that the combustion tube is much smaller and copper oxide is used instead of platinized quartz. The apparatus as used in the experiment herein described consisted of a combustion tube 70 cm. long and 9 mm. inside diameter.

The furnace is heated quickly and cools quickly; this means a great saving of time. The heat applied is not great enough to bend the tube. About the only disadvantage found was that it was deemed necessary by the authors to remove all the copper oxide every time a combustion was made. But even this is not necessary; one need remove only sufficient copper oxide to mix with the substance, and to rinse the tube. The introduction of the sample by means of a porcelain boat is, however, much simpler still. This simple furnace is perfectly satisfactory for all purposes of ordinary combustion.

The substances used in conducting the experiments were acetanilide and aniline.

1. Compare Proceed. Royal Soc. of Edinburg, vol. 28, p. 708.

The following are the theoretical values for carbon, hydrogen and nitrogen:

SUBSTANCE.	Per cent C.	Per cent H.	Per cent N.
Acetanilide.....	71.05	6.73	10.32
Aniline.....	77.35	7.58	15.05

About one-third of the results obtained in becoming familiar with the methods were outside the limit of accepted values, and no record was made of these, with the exception of Dennstedt's method, where all the results are recorded:

The following are results obtained by the usual method:

SUBSTANCE.	Weight.	Per cent C.	Per cent H.	Per cent N.
Acetanilide.....	0.1799	71.18	6.83	.....
Acetanilide.....	0.2204	71.20	6.96	.....
Acetanilide.....	0.1360	.....	.....	10.38
Acetanilide.....	0.1476	.....	.....	10.26
Aniline.....	0.1411	77.28	7.62	.....
Aniline.....	0.2156	77.29	7.67	.....
Aniline.....	0.1271	.....	.....	14.93
Aniline.....	0.1296	.....	.....	14.94

These results are taken from determinations made at an earlier time, and no record was kept of the time of each combustion.

Results obtained are as follows for each of the processes tested:

METHOD.	Substance.	Weight.	Per cent C.	Per cent H.	Per cent N.	Time.
Dennstedt.....	Acetanilide.....	.1206g	70.04	7.76	6.07	2:45
Dennstedt.....	Acetanilide.....	.1143g	70.07	6.98	6.22	1:50
Dennstedt.....	Acetanilide.....	.0703g	70.71	7.04	6.22	2:10
Dennstedt.....	Acetanilide.....	.0702g	71.03	7.05	6.17	2:05
Dennstedt.....	Acetanilide.....	.1428g	70.54	6.93	6.33	2:25
Dennstedt.....	Acetanilide.....	.0948g	68.14	7.94	5.59	3:20
Morse.....	Acetanilide.....	.0968g	71.03	6.70	.....	0:50
Morse.....	Acetanilide.....	.1108g	71.17	6.85	.....	0:45
Morse.....	Acetanilide.....	.1049g	70.91	6.94	.....	0:45
Morse.....	Aniline.....	.0891g	77.22	7.67	.....	0:50
Morse.....	Aniline.....	.1292g	77.37	7.63	.....	1:10
Morse.....	Aniline.....	.1232g	77.21	7.69	.....	1:05
Walker.....	Acetanilide.....	.1608g	70.98	6.78	.....	1:05
Walker.....	Acetanilide.....	.1884g	70.93	6.89	.....	1:10
Walker.....	Acetanilide.....	.1158g	70.84	6.73	.....	0:50
Walker.....	Acetanilide.....	.2319g	70.94	6.66	.....	1:15
Walker.....	Acetanilide.....	.1597g	70.85	6.71	.....	1:10
Walker.....	Acetanilide.....	.1591g	.....	.....	10.33	1:05
Walker.....	Acetanilide.....	.1029g	.....	.....	10.21	0:50
Walker.....	Acetanilide.....	.1594g	.....	.....	10.27	0:55
Walker.....	Aniline.....	.1551g	77.27	7.68	.....	0:50
Walker.....	Aniline.....	.1383g	77.29	7.58	.....	0:45
Walker.....	Aniline.....	.1021g	77.33	7.64	.....	0:40
Walker.....	Aniline.....	.1494g	.....	.....	15.09	0:55
Walker.....	Aniline.....	.1471g	.....	.....	15.01	0:45